

Bulk Crystal Growth of Piezoelectric PMN-PT Crystals Using Gradient Freeze Technique for Improved SHM Sensors

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ABSTRACT

There has been a growing interest in recent years in lead based perovskite ferroelectric and relaxor ferroelectric solid solutions because of their excellent dielectric, piezoelectric and electrostrictive properties that make them very attractive for various sensing, actuating and structural health monitoring (SHM) applications. We are interested in the development of highly sensitive and efficient PMN-PT sensors based on large single crystals for the structural health monitoring of composite materials that may be used in future spacecrafts. Highly sensitive sensors are needed for detection of defects in these materials because they often tend to fail by distributed and interacting damage modes and much of the damage occurs beneath the top surface of the laminate and not detectable by visual inspection. Research is being carried out for various combinations of solid solutions for PMN-PT piezoelectric materials and bigger size crystals are being sought for improved sensor applications. Single crystals of this material are of interest for sensor applications because of their high piezoelectric coefficient (d_{33} greater than 1700 pC/N) and electromechanical coefficients (k_{33} greater than 0.90). For comparison, the commonly used piezoelectric ceramic lead zirconate titanate (PZT) has a d_{33} of about 600 pC/N and electromechanical coefficients k_{33} of about 0.75. At the present time, these piezoelectric relaxor crystals are grown by high temperature flux growth method and the size of these crystals are rather small ($\sim 3 \times 4 \times 5$ mm³). In the present paper, we have attempted to grow bulk single crystals of PMN-PT in a 2 inch diameter platinum crucible and successfully grown a large size crystal of 67%PMN-33%PT using the vertical gradient freeze technique with no flux. Piezoelectric properties of the grown crystals are investigated. PMN-PT plates show excellent piezoelectric properties. Samples were poled under an applied electric field of 5 kV/cm. Dielectric properties at a frequency of 1 kHz are examined. The grown PMN-PT crystals show typical relaxor dielectric properties. Additionally, the thermal properties of the sample are tested. The results are in good agreement with those found in the literature and some are reported for the first time.

1. Introduction

Structural health monitoring is a broad engineering research topic and a variety of sensors and smart materials will need to be integrated in the structure of the system for effective results. For getting highly sensitive devices, processing materials into bulk single crystals will be required for eventual use for this application. Piezoelectric materials exhibit strong coupling between electrical and mechanical energy, and thus have been widely used in many technological fields, such as ultrasonic transducers, actuators, ultrasonic motors, and structural health monitoring. The answer to the improvement of overall properties in the piezoelectric materials is single crystals. The developed piezoelectric single crystals offer field induced strain as an order magnitude higher than what can be achieved in piezoelectric ceramics. Furthermore, the strain electric field hysteresis and dielectric properties are improved.

If one were to choose the most difficult problem in the domain of structural health monitoring it would probably be the assessment of wear and tear on a Lunar habitat. Being constantly eroded by meteorites and attempting to estimate the remaining useful life of the structure. The arena of monitoring the state of health of structural systems is rapidly expanding and newer technologies and techniques are forthcoming rapidly. These techniques represent systems beyond typical sensors that glue to the surface of a structure or attach externally in some other manner. Also, the problem has become more subtle in that the prognostics must be more accurate due to the fact that re-work will be more difficult and much more time consuming. For instance, the lunar habitat will be very difficult to replace; therefore, the prognostics must be more accurate to achieve the greatest life without unduly increasing the risk of becoming unsafe and un-repairable simultaneously. A lunar habitat wear-out sensing system is needed that is not only robust within its' own structure, but must be highly dependable in its ability to ascertain the remaining life before "punch through" and loss of atmosphere may occur. One of the more novel approaches to accomplish this will be addressed by this paper.

The tough requirement for a fully embedded lunar habitat structural health monitoring system is that one should not be able to perceive its presence by external appearance and it should not, itself, be vulnerable to the phenomenon of micrometeorites that it is attempting to sense. Also, it should have no wiring for either power or signal making it totally passive and thus more robust in nature. The sensor elements described in this paper have the property that, when stressed, even shocked by a mechanical impulse or "hit", then give off a flash of light. Therefore, by coating the undersurface of the lunar habitat, one can monitor "impulse shocks" by merely monitoring the light emissions. This would be somewhat like monitoring lightning strikes in a particular geographic region of the earth by observing from space in low earth orbit. This is a technique employed by the weather monitoring systems routinely. For the Lunar habitat, one could place a "fish eye" camera at a strategic location where it could monitor the entire area of the interior of the habitat. The bottom line would be a system that would feature the intrinsic properties of passive robustness along with precision accuracy.

In our previous attempt, single crystals of $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.33PbTiO_3 (abbreviated as PMN-PT (67/33)) were grown in our laboratory with high quality, but small size using the high temperature flux method [1]. Here, large sized PMN-PT single crystals are grown from the vertical gradient freeze method with no flux. In this publication, the details of no flux method along with the results of a systematic study of piezoelectric and dielectric properties of the obtained crystals are presented.

2. Experimental Procedure

Single crystals of lead magnesium niobate-lead titanate (PMN-PT) with the chemical structural formula $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 in the ratio 67:33 were synthesized using stoichiometric amounts of the high purity materials: PbO , MgO , Nb_2O_5 and TiO_2 . Raw powders were weighed with desired molar ratios. The initial weights for a charge of one mole of PMN-PT solid solutions (volume density equals 8.2 g/cm^3) were calculated to be consisted of 8.96 g of MgO , 59.10 g of Nb_2O_5 , 26.63 g of TiO_2 and 223.19 g of PbO . The dry powders were mixed for a desired period of time using a tumbling mill.

The vertical gradient freeze method with no flux was used to obtain PMN-PT single crystals. The system PMN-PT (67/33) was loaded in a platinum crucible covered with an alumina lid. Due to high volatility of PbO , the crucible was sealed by means of alumina cement. The crystal growth was carried out in a cylindrical furnace equipped with a programmable temperature controller (Figure 1).

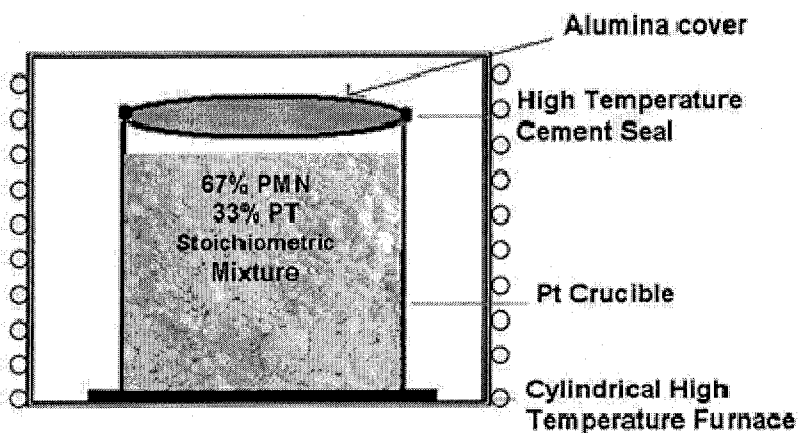


Figure 1. A Pt crucible used in the growth of PMN-PT single crystals from the vertical gradient freeze method with no flux.

An optimized thermal profile was used for the growth of PMN-PT crystals as illustrated in Figure 2 by spontaneous nucleation, namely: (i) heating from room temperature to 900°C at a ramp rate of 150°C/h and dwelling for 6 h; (ii) heating at 100°C/h to 1310°C and dwelling for 24 h; (iii) slow cooling from 1310°C to 1100°C at 2°C/h , from 1100°C to 1000°C at 3°C/h , from 1000°C to 800°C at 5°C/h , then from 800°C down to room temperature at 20°C/h . This slow cooling process was applied to obtain a more stable growth.

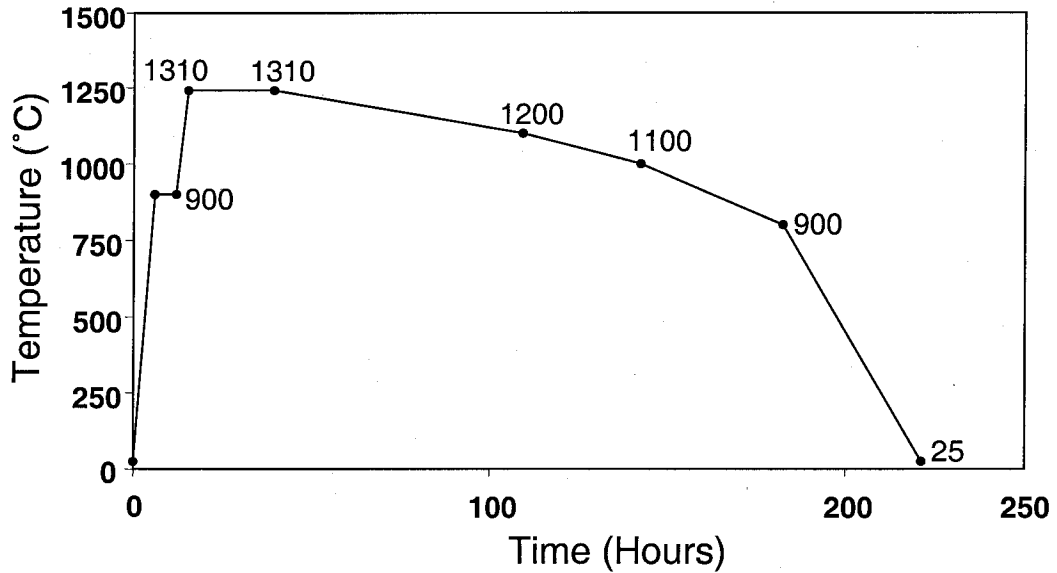


Figure 2. Thermal profile used in the growth of PMN-PT single crystals from the vertical gradient freeze method with no flux.

In order to get bigger sized PMN-PT single crystals, the growth process was repeated for three times. In each time, a lead loss of about 1 wt% was observed by checking the weight difference before and after growth run. To overcome this problem, 1 wt% of excess PbO was added to the charge to compensate the lead loss.

Piezoelectric properties of PMN-PT single crystals were measured using a d_{33} meter from/KCF, model A-3001. For piezoelectric charge determination, two bar shaped samples with a length ranging from 3 to 5 mm were tested. The two samples were poled by applying an electric field of 5 kV/cm for a desired period of time at room temperature. Both the real and imaginary parts of the dielectric constant for a poled sample of an PMN-PT single crystal with dimensions of $9.2 \times 7.5 \times 1.13 \text{ mm}^3$ at a frequency of 1 kHz were measured as a function of temperature. The sample was heated to around 215°C and the temperature dependence of the dielectric data was measured at a rate of $3^\circ\text{C}/\text{min}$ as well as the value of electrical capacitance. Values of dielectric constant and dielectric loss were then calculated for each value of the capacitance. Finally, thermal analysis was performed by simultaneous differential calorimetry and thermogravimetric analysis (SDT 2960). A specimen (as grown crystal) of about 20 mg each was put in an alumina pan and heated from room temperature to 1350°C at a rate of $20^\circ\text{C}/\text{min}$ in an air atmosphere. The thermal conductivity k was estimated from the following relation:

$$k = \alpha C_p \rho$$

where C_p is the specific heat at constant pressure, ρ is the density and α is the linear thermal coefficient (thermal diffusivity).

3. Results and discussion

Several regular cubic-shaped PMN-PT crystals were clustered near the top surface around the edge of the crucible. Figure 3 shows a top-view of an as grown crystal inside a platinum crucible. Except for the top layer, entire solid has been crystallized in a single crystal.



Figure 3. A top view of an as-cooled Pt crucible showing the growth of PMN-PT (67/33) single crystals.

In the first run, several crystals were found to be grown at the wall and at the center of the crucible. Most of the crystals were found on the inside wall and bottom of the platinum crucible. Their size approximately varied from 0.3 to 0.5 cm³. On the other hand, lots of smaller crystals with well-developed rectangular shapes were found at the bottom and in the center of the crucible. Crystals which presented near the walls of the crucible were smaller in size and have been observed with green color, whereas crystals found at the centre of the crucible had lighter green color. This difference in color is expected either due to the presence of pyrochlore phase or due to difference in the composition. In the third run, the size of the obtained crystals grown by present method was much larger relatively and varied from 1 to 4 cm³. A selected PMN-PT single crystal with a large size is shown in Figure 4. The crystal was cut and well polished to achieve flat and parallel surfaces for characterization purposes.

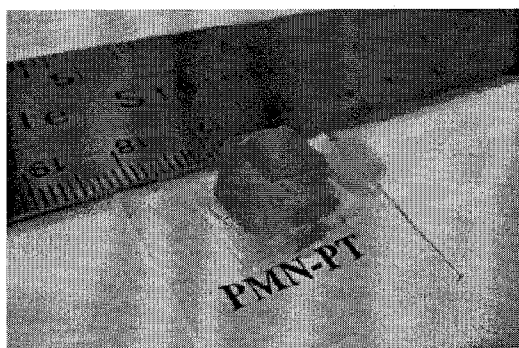


Figure 4. A cut and well polished PMN-PT single crystal grown from the vertical gradient freeze method.

The obtained values of d_{33} before and after poling are shown in Table 1 below. These values of piezoelectric charge are quite high as compared to the previous reported values[2]. In fact, the piezoelectric properties of PMN-PT crystals fluctuated somewhat for either the different plates or different points on the same plate, which might arise from the macroscopical segregation in compositions, the fluctuation in structures and the existence of structural defects and space charge field.

Table 1 d_{33} values for two different samples of an PMN-PT single crystal before and after poling by an electric field of 5 kV/cm at room temperature:

SAMPLE	d_{33} (Before Poling) (pC/N)	d_{33} (After Poling) (pC/N)
1	26	850
2	25	945

The dielectric measurements for the grown crystals indicated a relaxor type ferroelectric phase transition behavior. The dielectric constant increased gradually with temperature increasing up to the transition temperature, then rapidly decreased as the temperature further increases. The multiple transitions in the single crystal, which changes from rhombohedral (R) ferroelectric, through tetragonal (T) ferroelectric, to cubic paraelectric phases, have been observed through the dielectric, piezoelectric and elastic properties as function of temperature. Two temperature peaks were observed. The lower one is the transition between rhombohedral phase and the tetragonal phase, whereas the higher temperature peak is considered to be the phase transition temperature (Curie temperature T_C). T_C is the transition between the tetragonal phase and the cubic phase. The value of the dielectric constant is 4718 at the transition temperature T_{RT} of 87.5°C between the rhombohedral phase and the tetragonal phase. The dielectric constant has a maximum value of 11843 at the transition temperature T_C of 159.4°C between the tetragonal phase and the cubic phase. T_C is defined as the temperature of the maximal dielectric constant ϵ' at 1 kHz.

The DSC/TGA results for the PMN-PT crystals are shown in Figure 5. A strong endothermic DSC peak was detected at 1264.12°C, which indicated to the PMN-PT melting point. Around the melting point, a negligible amount of the original mass of the sample was lost by stimulation.

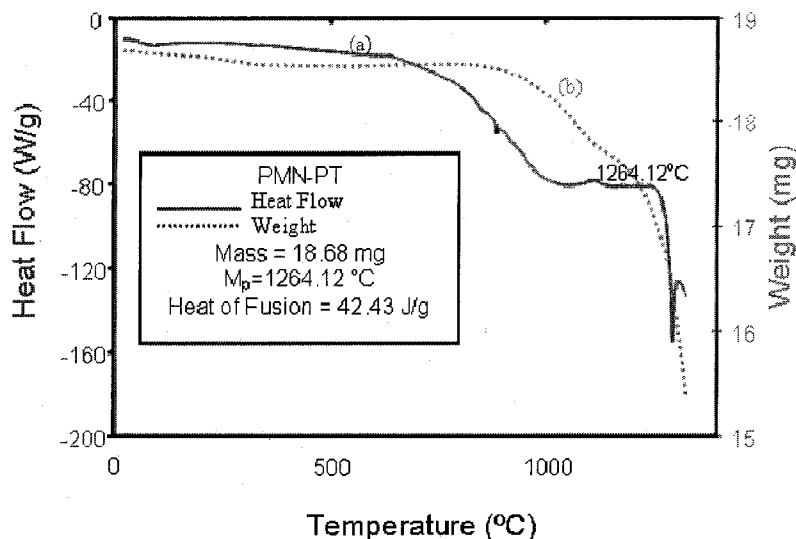


Figure 5. A DSC-TGA plot for a PMN-PT single crystal showing the melting peak (a) and the weight loss (b).

For the thermal conductivity measurement, values of the density and the linear thermal coefficient (thermal diffusivity) for $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.33\text{PbTiO}_3$ single crystals were found from literature to be $4.4 \times 10^{-3} \text{ cm}^2/\text{s}$ and 8.2 g/cm^3 respectively. A C_p value of 0.4 J/g.K was estimated by calibrating our SDT measurements against literature data for Al_2O_3 (sapphire). The value of thermal conductivity k was then calculated to be 0.014 W/cm.K .

4. Conclusion

Big sized single crystals of $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.33\text{PbTiO}_3$ of perovskite structure were successfully grown from the vertical gradient freeze method with no flux. The d_{33} values for two different samples of an PMN-PT single crystal were measured before and after poling by an applied electric field of 5 kV/cm at room temperature. PMN-PT plates showed excellent piezoelectric properties with d_{33} values larger than 940 pC/N . The temperature dependence of the dielectric constant for a poled sample was studied at a rate of 3°C/min and a frequency of 1 kHz . The grown PMN-PT single crystals showed typical relaxor dielectric properties with broad peak. The dielectric constant was found to be 11843 at Curie temperature. Multiple transitions in the single crystal have been observed. The higher temperature peak considered to be the phase transition temperature (Curie temperature) and measured to be 159.4°C . Finally, the thermophysical properties of the sample were measured. A few of the results were in good agreement with those found in the literature and some were reported for the first time.

Acknowledgements

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